COST Action CM1104
REDUCIBLE OXIDE CHEMISTRY, STRUCTURE AND FUNCTIONS

WG3 MEETING
Adam Mickiewicz University, Poznan


ABSTRACTS
Active ceria nanoparticles without vacancies

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INTRODUCTION
Ceria is a technologically interesting material with numerous application areas [1]. In most practical applications, the high interest originates from the remarkable redox properties of ceria resulting in a very rich and variable oxygen chemistry. In the past, this oxygen chemistry has mainly focused on lattice oxygen and oxygen vacancies. These are certainly relevant for high temperature applications involving ceria, such as the three-way catalyst for automotive exhaust purification [1]. However, their role in low temperature applications, such as nano-medicine [2], is less clear, mainly owing to the relatively high vacancy formation energy. Instead, at low temperature, other redox routes must be accessible. Small ceria nanoparticles (CNP’s), with diameter smaller than 5nm, have been shown to display a dramatically increased oxygen storage capacity (OSC) [3]. In the current presentation, the origin of this phenomena and it’s connection to low temperature redox chemistry is discussed based on the results of recent theoretical simulations[4-5].

METHOD
All Density functional theory (DFT) calculations presented here were done using the software package Vienna Ab-initio Simulation Package (VASP) while self-consistent charge density functional tight binding (SCC-DFTB) calculations were performed using the DFTB+ code with our own custom made parameters for ceria. SCC-DFTB is an approximate DFT approach derived from a second-order expansion of the DFT energy with respect to charge density fluctuations.

RESULTS & DISCUSSION
We have explored the stability and energetics of reactive oxygen species (ROS) and how they may form on the surface and bulk of ceria [3] and on small models of ceria nanoparticles (CNPs) [4]. Our DFT calculations shows that cerium rich, and hence partially reduced, CNP’s are stabilized in oxidative atmosphere through a strong interaction with O$_2$ molecules leading to the formation of superoxide species (O$_2^-$). This in turn results in oxygen rich particles, supercharged CNPs, which explain the dramatically increased OSC found for small CNP’s. Recent experimental findings [6] provide support for our proposed mechanism. Besides the increased OSC for small CNP’s, the reduced size opens up for low-temperature redox chemistry without the formation of explicit oxygen vacancies. I will present our current understanding of supercharging in CNP’s, based on our previous DFT calculations on simple model structures and expand further how we can use the SCC-DFTB method to study these phenomena in more complex structures, such as ceria nanocubes, nanowires etc.

Supported metal nanoparticles are frequently used as models of heterogeneous catalysts, with behaviour thought to be dependent on the nanoparticle size. Above a certain size it has generally been assumed that the nanoparticle behaves in the same way towards adsorbates as would a semi-infinite crystal. In this work, we examine this proposition using CO adsorption on Pd nanoparticles supported on TiO$_2$(110) using scanning tunnelling microscopy. The results show that the CO lateral registry differs from the single crystal. This phenomenon arises from a curvature of the nanoparticle that is caused by the underlying substrate step-edges. At a CO coverage of half a monolayer, two types of CO adlayer form in addition to those observed on the native Pd(111) surface. Density functional theory calculations suggest that their formation is driven by curvature-related strain.
Synthesis, characterization and catalytic application of nanoporous silicas co-condensed or grafted with aminosilanes

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Ordered mesoporous silicas are objects of intensive studies due to their specific textural and structural parameters as well as a broad range of potential applications. Additionally, the incorporation of amino groups changes a relatively inert character of silica surface and creates acid-base sites, what facilitates the use of silica-based nanomaterials in a broader range of applications (catalysis, adsorption, sensors, etc.) [1-3].

The aim of the presented studies was to develop the efficient synthetic procedures to obtain ordered nonporous silicas with amino functionalities. Amino groups were introduced by so called "one-pot" technique as well as by “grafting” procedure, where the first one is based on direct synthesis of modified materials, whereas the latter comprises of the post-synthetic step, where amino groups are grafted on the surface of silica. Moreover, the amino-modified nanoporous silicate materials were synthesized in the form of powders and self-standing films.

In a typical synthetic procedure TEOS (tetraethyl orthosilicate) and Z6032 aminosilane (vinyl-benzyl-aminoethyl-aminopropyl-trimethoxysilane) were used as a silicon and amino source, respectively. Two different triblock co-polymers were applied as structure directing agents, namely Pluronic P123 in the case of SBA-15 and Pluronic F127 in the synthesis of SBA-16 materials. Template removal proceeded with calcination (pure siliceous samples) or extraction technique (amino-modified materials).

All synthesized materials were subjected to low-angle XRD measurements and TEM analysis in order to confirm their ordered mesoporous structure with hexagonal (SBA-15) or regular (SBA-16) arrangement of pores. Textural parameters were calculated on the basis of low-temperature nitrogen sorption measurements. Incorporation of amino groups was confirmed by elemental analysis as well as FT-IR measurements. Procedures applied for template removal enabled preservation of nanoporous structures in both films and powder materials. Catalytic test, performed with Knoevenagel condensation between ethyl acetylacetonate and benzoaldehyde, indicated that synthesized materials may be used as effective catalysts in this reaction, resulting in 95% selectivity to the desired product.

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Near-Ambient XPS Characterization of Interfacial Copper Species in Ceria-Supported Copper Catalysts

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Catalysts combining copper and cerium oxides are an economically interesting alternative to noble metal catalysts for various processes involved during production-purification of hydrogen generated from hydrocarbons or biomass. In particular, they show promising characteristics for processes involving CO oxidation like the water-gas shift reaction (WGS) or preferential oxidation of CO (CO-PROX). Their catalytic properties for such processes depend strongly on the characteristics of the interface formed between the two oxide components \[1,2\]. However, direct information on interfacial properties is not generally available due to the important difficulties for the isolation and characterization of such nanosized generally amorphous region. The present contribution explores these issues by means of near-ambient XPS spectroscopy (and Cu L\textsubscript{3} XANES) complemented with theoretical DFT analysis. Two samples of copper oxide dispersed on two different ceria supports (in the form of nanospheres –NS– and nanocubes –NC–, respectively), which allow comparison between well differentiated situations in terms of degree of dispersion and interfacial morphology, are employed for this purpose. Direct evidence of reduced interfacial copper entities, considered as active sites for CO oxidation in this type of catalysts \[1,2\], as well as significant details of the electronic properties of the dispersed partially reduced copper oxide entities are provided by detailed analysis of the results obtained.

Details of the preparation and multitechnique (XRD, HREM, Raman, XPS, EPR, H\textsubscript{2}-TPR, S\textsubscript{BET}) characterization of the two catalysts can be found elsewhere \[3\]. The catalysts subjected to treatment under diluted CO up to 300 °C or under model CO-PROX mixture (for which case a physical mixture of the catalyst with conducting inert material is used as an strategy to avoid charging effects during recording of the spectra) are examined by XPS in gas environment (100 Pa) obtained at the BESSY II synchrotron in Berlin. Figure 1 provides an example of the results obtained. New XPS Cu 2p\textsubscript{3/2} (at 930.1 eV) and Auger L\textsubscript{3}M\textsubscript{45}M\textsubscript{45} signals (at ca. 913 eV) specific of interfacial Cu\textsuperscript{+} entities are identified on the basis of theoretical analysis and consideration of respective amount and characteristics of the interfacial sites present in each sample \[3\]. The evolution of the chemical state of the various copper species as a function of the reduction temperature under CO or during treatment under CO-PROX mixture will be shown and discussed in the context of the catalytic properties of this type of systems.

Tuning the Reactivity of Ultra-Thin Oxides: NO Adsorption on Monolayer FeO(111)

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Temperature-programmed desorption, reflection absorption infrared spectroscopy and low energy electron diffraction measurements show that NO adsorbs on ultrathin FeO(111) films supported by Ag(100), leading to a (1 x 1) structure that is stable up to room temperature. The result is in sharp contrast to adsorption over Pt(111) supported FeO(111), where NO does not adsorb above 100 K. The decisive effect of the support metal on the adsorption process is corroborated by density functional theory calculations showing that NO adsorption on the Pt(111)-supported film is kinetically hindered by a barrier that is absent for Ag(100)-supported FeO(111). This barrier originates from rumpling of the film which causes electrostatic repulsion between NO and oxygen anions. The results demonstrate the possibility to tune the chemical reactivity of ultra-thin oxide films through purely steric effects.

References

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Simulations by density functional method of IR vibrational frequencies of CO adsorbed on isolated platinum species and platinum species supported on ceria

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Our periodic density functional calculations of various Pt-containing models helped to confirm and clarify assignments of various bands detected experimentally when CO is adsorbed on Pt/CeO2 samples [1,2]. The calculations also predicted where the IR bands of CO molecules with certain coordination environment are to be found. For instance, bridged coordinated CO on Pt is expected to have a band at 1840-1885 cm−1. Linearly adsorbed CO to Pt0 should have a band in the region 2018-2077 cm−1, depending on the coordination number (CN) of Pt atoms, CN = 2 to 9. As a trend the lower the CN is, the lower the C-O vibrational frequency, ν(C-O), is. The flexibility of the Pt surface can also influence the C-O vibrational frequencies, as more flexible surfaces bind CO stronger and shift C-O vibration to lower frequencies.

When is CO adsorbed on Pt atoms supported on stoichiometric ceria, the ν(C-O) values are in the range 2010-2032 cm−1. The frequency does not change notably at reductive conditions, when one or two O vacancies are created. However, at oxidative condition, when one or two O atoms are added to the Pt atom, the C-O vibration features notably higher frequencies: ν(CO) values are 2043-2077 cm−1 and 2095-2121 cm−1 for CO adsorption on Pt2+ and Pt4+. Pt2+ species form very stable square planar dicarbonyl complexes with frequencies at: 2066-2086 (antisymmetric) and 2115-2142 (symmetric) cm−1.

Spillover of one O atom from ceria support to the small Pt clusters does not change notably the adsorption energy of the CO and its vibrational frequency, but when oxygen coverage increases the adsorption energy of CO is reduced and the CO vibration is shifted to higher frequencies.

At reductive conditions the most stable sites for mononuclear Pt species are at small (100) facets. The same sites are the most stable for PtO species, while at strongly oxidative conditions for PtO2 the most stable positions are at (111) facets [3]. When CO is adsorbed, the preferred adsorption sites are interchanged: at reductive conditions preferred positions of the PtCO complexes are at (111) facets, while at oxidative conditions preferred positions of the PtOCO complexes are at the small (100) facets. At the reductive conditions CO can pull out Pt species from the most stable positions at (100) facets, hence making Pt more reactive, while at the oxidative conditions Pt species stays upon CO adsorption in the same position.

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References
Metallic and oxidic Pt, Pd and Ni deposits on CeO$_2$(111): metal oxide interactions, stability and charge transfer

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Electronic interactions between metal nanoparticles and oxide supports control the stability, the activity, and the selectivity of numerous catalytic materials. Such interactions are accompanied by electron transfer across the metal particle/support interface or redox processes involving the metal deposit. Here, we present recent results of three related model studies, which originate from the cooperation of four workgroups within the COST Action CM1104.[1-3]

In the first study, we have quantified the charge transfer between metallic Pt nanoparticles and the ceria support over a broad range of particle sizes.[1] Combining synchrotron-radiation photoelectron spectroscopy, scanning tunneling microscopy, and density functional calculations we show that the charge transfer per Pt atom is largest for Pt particles of around 50 atoms. Here, approximately 1 electron is transferred per 10 Pt atoms from the nanoparticle to the support. For larger particles, charge transfer reaches its intrinsic limit set by the support. For smaller particles charge transfer is partially suppressed by nucleation at defects. Depending on its surface structure, Pt can be stabilized on CeO$_2$ not only in metallic form but also in the form of dispersed Pt$^{2+}$.[2] We have investigated the reactivity of this atomically dispersed Pt$^{2+}$ species on CeO$_2$ films and the related mechanism of H$_2$ activation. Isolated Pt$^{2+}$ sites are found to be inactive towards H$_2$ dissociation. Trace amounts of metallic Pt are necessary to initiate H$_2$ dissociation on Pt–CeO$_2$ films. H$_2$ dissociation triggers the reduction of Ce$^{4+}$ cations which, in turn, is coupled with the reduction of Pt$^{2+}$. Pt$^{2+}$ reduction involves reverse oxygen spill-over and formation of oxygen vacancies on Pt–CeO$_2$ films, above a critical threshold concentration.

Finally, we have compared the stability and the reactivity of atomically dispersed Pt, Pd, and Ni species on CeO$_2$.[3] All three metals resemble specific similarities which are associated with the large adsorption energy of atomically dispersed Pt$^{2+}$, Pd$^{2+}$, and Ni$^{2+}$ species and exceed the corresponding cohesive energies of the bulk metals. Corresponding Pt–CeO$_2$, Pd–CeO$_2$, and Ni–CeO$_2$ model catalysts have been prepared in the form of thin films on CeO$_2$(111). Indeed, the atomically dispersed Pt$^{2+}$, Pd$^{2+}$, Ni$^{2+}$ species were formed at low dopant concentration. High dopant concentration resulted in the formation of additional oxide phases and the emergence of metallic nanoparticles. With respect to its redox behaviour, the properties of Pd–CeO$_2$ films closely resembled those of the Pt–CeO$_2$ upon reaction with hydrogen. In contrast to Pt–CeO$_2$, Pd–CeO$_2$ shows a strong tendency to stabilize Pd$^{2+}$ not only at the surface but also in the ceria bulk.

Dopant size dependence on the activation of methane in alkali metal doping of the CeO$_2$ (111) surface

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Biogas is obtained from the breakdown of organic matter and is a highly attractive prospect as a renewable energy source for biofuel production. It primarily constitutes of methane gas (CH$_4$) mixing with minor amounts of CO$_2$, H$_2$S and siloxanes. Biogas can be used to create synthetic gas (syngas, CO + H$_2$), a precursor to methanol (CH$_3$OH) and higher alkane (biodiesel) production.\textsuperscript{1,2} The difficulty with using biogas however, lies in activating CH$_4$ due to the high bond dissociation energy of 435 kJ/mol for breaking the first C-H bond in the gas phase. The rate limiting step in the production of syngas is the scission the first CH bond of CH$_4$, and in order to facilitate this large energy requirement, a catalyst is needed to reduce the activation barrier.\textsuperscript{3}

Cerium dioxide (CeO$_2$) is a well-known highly reducible oxide with numerous applications in heterogeneous catalysis. The (111) facet is the most thermodynamically favorable surface, and hence most expressed during reaction conditions. Substitutional cation doping of the surface is generally found to increase the reactivity, in particular dopants which have a +2 oxidation state in their parent oxides. These dopants spontaneously cause oxygen vacancies to form and thus increase the oxygen mobility at the surface interface, which is an important property for partial oxidative coupling of methane gas. Density functional theory calculations are used to investigate methane activation by using alkali metals (Mg, Ca, Sr) to modify the (111) surface of CeO$_2$ to improve C-H bond dissociation. The calculations indicate that the thermodynamic drive to dissociate CH$_4$ to CH$_3^+$+H becomes less favorable with increasing dopant size. The kinetic barriers are seen to be reduced by this trend in accordance with the Bronsted-Evans-Polanyi relation, indicating that the methane activation rate improves with increased cation size. Additionally, a study of the removal of a second oxygen species known as the ‘active oxygen vacancy’ plotted against the adsorption energy of the dissociated species shows a linear response suggesting that the active Ovac can be used as a descriptor for future catalyst design.


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Introduction
Fe-doped NiOOH, a highly active co-catalyst for O₂ evolution in photoelectrochemical water splitting [1], is not well understood since its structure, with H-bond linked layers, is normally highly disordered. Here this system, Fe-doped or not, is modelled with a hybrid DFT method, and its band alignment with a typical visible light active photocatalyst, BiVO₄, is studied.

Methods
VASP code was used for hybrid DFT calculations using a method that gives accurate bandgaps [2] and where the Fock exchange fraction is related to the optical dielectric constant. Band offsets were computed with periodic slab models using electrostatic potential as basis to which band edge positions were referenced [3].

Results & discussion
Several of the NiOOH sheet stackings and proton arrangements evaluated yielded similar lowest energies, justifying the typical high disorder of this material. Centrosymmetric NiO₆(OH)₆⁻n arrangements seem preferred to the average NiO₃(OH)₃ environment. Even n=0 gives some of such lowest energies; in that case disproportionation into Ni⁴⁺ and Ni²⁺ occurs. Bandgaps typically above 0.8 eV are found, the gap edges being formed mainly by Ni (3d) orbitals.

Substitution of Ni by Fe leads to filled Fe(3d) levels near the valence band edge (Fig. 1). In some configurations a redox process Ni³⁺ + Fe³⁺ -> Ni²⁺ + Fe⁴⁺ occurs, eventually with jump of protons from Fe to Ni coordination spheres. This justifies experimentally observed high conductivities and may be important for the photoelectrochemical O₂ formation mechanism from water.

The band alignment study (Fig. 2) indicates that holes generated at the BiVO₄ photocatalyst can be transferred easily to the NiOOH valence band, where they may oxidize surface OH to O₂.

References
Dependence of the charge transfer at the Rh-CeO$_x$ interface on the stoichiometry of cerium oxide (2.00 > x > 1.67)

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The electronic metal substrate interaction (EMSI) plays an important role in the chemistry of supported nanoparticles. Even small perturbations caused by an electron exchange between the particle and the substrate, local electric fields generated by exposed ions of the support, or morphological changes due to the interaction with the surface may have a great impact on the reactivity and catalytic activity of the metal clusters [1]. Significant differences in the oxidizing ability were reported for the rhodium particles supported by highly oxidized and reduced cerium oxide substrates [2]; and it was suggested that the EMSI is responsible for this phenomenon.

We present a combined experimental and theoretical study focused on the interaction between rhodium and cerium oxide with various stoichiometries. The Rh-CeO$_x$ interaction was investigated by means of the photoelectron spectroscopy for 2.00 > x > 1.67. When depositing rhodium, we observed the reduction or oxidation of cerium oxide substrate, depending on its initial stoichiometry (Figure 1). Additionally, the DFT+U simulations of the rhodium adatom adsorbed on the CeO$_2$(111) surface and the oxygen vacancy showed that a charge transfer would occur at the Rh-CeO$_x$ interface. Different directions of the charge transfer were calculated for Rh adsorbed on the stoichiometric CeO$_2$ and on the oxygen vacancy (Figure 2).

Our results demonstrate that there are two different kinds of EMSI at the Rh-CeO$_x$ system, depending on the stoichiometry of CeO$_x$. These results therefore support the suggested interpretations of different oxidizing mechanisms on Rh-CeO$_x$ showing a great impact of the electronic metal substrate interaction on the chemistry of the system.

Figure 1: The evolution of the degree of cerium oxide reduction during consecutive deposition of rhodium onto CeO$_x$ with various initial stoichiometries.

Figure 2: Change of Rh-CeO$_x$ bonding charge integrated in planes perpendicular to the surface plotted as a function of the height from the surface.

Recent progress in density functional studies of ceria-based nanostructures: Inspiration by experimentalists from Erlangen and Prague

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We overview recent results of our density functional modelling of ceria-based nanostructures relevant for catalytic applications. Most of these studies have been inspired in the course of the COST Action by the groups of J. Libuda and V. Matolin and performed jointly with these teams of experimentalists.

Among the topics to be highlighted in the presentation are:

- Self-assembled ceria nanoparticles and oxygen vacancy formation energies in such systems [1].
- Most energetically stable structures of thin Ce₂O₃ films [2].
- Electron transfer from platinum particles deposited on ceria to the support [3].
- Calculated vs. measured Pt 4f core level shifts for ceria-supported particles of different size and structure.
- Reactivity of atomically dispersed Pt²⁺ species towards H₂ [4].
- Stability of transition metal species atomically dispersed at surfaces of nanostructured ceria as prospective single-metal catalysts [5, 6].

Figure. Pt nanoparticle supported on CeO₂(111).

References:

Metal-dependent versatility of the oxidation state and related CO oxidation performance of noble metal nanoparticles in interaction with ceria

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Due to its excellent redox properties, ceria is extensively used in heterogeneous catalysis, where it can act as an oxygen buffer in oxidation reactions or prevent coking of metal phases in hydrocarbon reforming reactions. In this work, ceria-supported platinum-group metal (Pt, Pd, Ir, Rh, Ru) nanoparticles were prepared in a single step by solution combustion synthesis, a simple and inexpensive method favoring metal-oxide interaction and thermal stability [1-3]. The powders were characterized by a variety of techniques (HRTEM, SEM, XRD, XPS, Raman spectroscopy, etc.) and systematically compared for CO oxidation and preferential CO oxidation in excess of hydrogen (PROX) in a flow-fixed-bed reactor. Ceria-supported Rh and Pt appear as the most efficient catalysts in CO oxidation (CO:O\textsubscript{2} = 2:2 mol% of 1 atm) and PROX (CO:O\textsubscript{2}:H\textsubscript{2} = 2:2:48 mol%), respectively [3]. These two systems, as well as pristine ceria, were further selected for a comparative operando DRIFTS-MS study, with particular focus on the effect of CO+O\textsubscript{2} conditions on the nature of the adsorbed species. Whereas the reaction starts above 150 °C on CeO\textsubscript{2} and Rh–CeO\textsubscript{2}, and does not depend on the state of the surface (i.e. pre-exposed to CO:O\textsubscript{2} 4:4 mol% or 7:1 mol% mixture), Pt–CeO\textsubscript{2} shows strong dependency on the initial state and substantial activity is achieved at much lower temperatures with the CO-rich feed (Fig. 1). On the basis of IR data, this result was related to a change in Pt oxidation state via strong interaction with ceria [4].

Figure 1. From left to right: HRTEM images of Pt–CeO\textsubscript{2} and Rh–CeO\textsubscript{2} catalysts, CO\textsubscript{2} formation rate during the last CO oxidation cycle for each system, and illustration of the experimental protocol.

B-site Pd and Ni promoted La$_{0.6}$Sr$_{0.4}$Co$_{1-x}$Fe$_{x-0.03}$M$_{0.03}$O$_{3-\delta}$ (x=0.2-0.8) perovskites: effect of composition on the structural properties

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Thanks to their mixed ionic/electronic conductivity and high catalytic activity for oxygen exchange reaction, La$_{1-x}$Sr$_x$Co$_{1-y}$Fe$_y$O$_{3-\delta}$ (LSCF) perovskites have received much attention as cathode materials for intermediate solid oxide fuel cells (IT-SOFCs) operating at relatively low-temperature, 600-800 °C. Lowering the operating temperature, however, decreases the electrode kinetics, in particular the oxygen reduction at the cathode.

It is widely accepted that the rate-limiting step of O$_2$ reduction process is the solid state diffusion of oxygen anions through the vacancies of the cathode lattice. LSCF oxides with metal substitution in B-site prepared by different methods, such as solid-state reaction or by impregnation of the perovskite with the metal dopant precursor, have been extensively investigated as new cathodes with enhanced oxygen reduction activity [1]. The promotion of redox properties of La$_{0.6}$Sr$_{0.4}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ and of La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ by incorporation of Pd$^{4+}$ into the B-site of the perovskite lattice, through one pot citrate synthesis, has been recently demonstrated by some of us [2]. The present work aims to get more insight into the B-site metal promotion by investigating the effect of two metals (Pd and Ni) and by using citrate-EDTA method which provides a good control of the microstructural properties.

Perovskites with compositions La$_{0.6}$Sr$_{0.4}$Co$_{1-x}$Fe$_{x-0.03}$M$_{0.03}$O$_{3-\delta}$ (x=0.2-0.8) doped with Pd and Ni have been prepared and compared with the un-promoted La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ and La$_{0.6}$Sr$_{0.4}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ materials. Characterizations by XRD, EXAFS, TPR, XPS, TGA, CO FT-IR, CO-TPD, EIS techniques have been carried out.

EXAFS analyses show that Ni$^{2+}$ is stabilized into the lattice of the perovskite or partially segregated as NiO as a function of the Fe content.

Addition of Pd and Ni to the LSCF perovskites influences in a different way surface and bulk properties.

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References

Interaction of Oxygen and Water Molecules with Fluorine Impurities at CeO$_2$(111)

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As some initial steps towards developing an understanding of the possible influence of F impurities upon the surface chemistry of ceria, we studied the interaction of such defects at the (111) facet with O$_2$ and H$_2$O. In experiments on commercially produced single crystalline samples of ceria, quantities of F impurities on the order of 7–10% in the near-surface region were detected [1]. On the other hand, deliberate doping of ceria with 10% F has also been achieved using a solution based method, and the resultant nanoparticles found to exhibit enhanced efficiency in oxidative coupling of benzylamines to imines [2], but the precise role of F was not determined. F impurities are n-type dopants, which lead to the formation of Ce$^{3+}$ ions in the lattice, and they might therefore be expected to enhance the redox chemistry of the material; however, the presence of F impurities/dopants might also lead to the formation of undesirable molecules such as F$_2$ and HF.

We used the VASP code [3], version 5.3.5, to carry out PBE+$U=5$ calculations using a (111) terminated CeO$_2$ slab of three-triple-layers thickness and a $p(5x5)$ surface supercell. For both molecules, we considered their interaction with an F impurity at the surface, as well as the possibility of extraction of the F to the gas phase, either as F$_2$ in the presence of O$_2$, or as HF in the presence of H$_2$O. We find that, in both cases, extraction of F to the gas phase is energetically unfavourable. Furthermore, we find that direct extraction of F as half an F$_2$ molecule under UHV is more energetically costly than extraction of lattice O as O$_2$, which can be understood in terms of the lesser stability of the F$_2$ molecule than that of O$_2$. At the surface, we find that an H$_2$O molecule displaces the F onto the surface and fills the vacancy thus formed, while in contrast, the O$_2$ molecule does not.

Thin oxide films grown on metal single-crystal substrates have been successfully used as suitable oxide supports for modeling highly dispersed metal catalysts at the atomic scale. Recent studies showed that ultrathin oxide films themselves may exhibit interesting properties, which may not be observed on thick films or single crystal surfaces. In addition to the films fully covering a metal support, enhanced reactivity may be observed at sub-monolayer oxide coverage due to the additional reaction pathway at the interface [1].

In this work, we studied CO oxidation on FeO(111) films grown on Pt(111) and Au(111) at sub-monolayer oxide coverages at both, ultra-high vacuum (UHV) and near-atmospheric pressure, conditions. The prepared model catalysts were characterized by LEED, AES, and TPD prior to and after reactivity measurements using GC in low temperature CO oxidation. The FeO(111) islands on Pt(111) are inert towards CO₂ formation. In contrast, the FeO₂₋ₓ trilayer structure, that only forms at elevated oxygen pressures, shows substantial CO₂ production that reaches a maximum at medium coverage at both, UHV and realistic, pressure conditions. The results corroborated by DFT calculations provide compelling evidence that the FeO₂₋ₓ/Pt(111) interface is the most active in CO oxidation. Although FeO₂₋ₓ boundaries possesses weakly bound oxygen species, strong binding of CO to Pt favors the reaction at the FeO₂₋ₓ/Pt interface as compared to the FeO₂₋ₓ/FeO one, thus giving a rationale to the reactivity enhancement observed in systems exposing metal/oxide boundaries, for example, ZnO/Pt. To see the role of CO as a second descriptor for reactions at the interface, FeO(111) films grown on Au(111) were studied, for comparison. The results clearly showed the support effects on the oxygen desorption behavior. DFT calculations are in progress.

Metal oxide catalysed selective oxidations: structure-activity aspects

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Reducible metal oxides are used as catalysts in many commercially important reactions. Structural features of such oxides strongly influence their catalytic performance. In this talk, I will present our results on selective oxidation of lower alkanes such as propane and butane and oxidation of biomass derivatives over transition metal oxides. In the former, we observed strong influence of basal planes of mixed oxides in determining the selectivity of oxidation products. Also, we have observed different phases of the same mixed oxide have different catalytic ability. Figure 1 shows an example of our results for butane oxidative dehydrogenation over one of the vanadate catalysts prepared in our laboratory. We observed that different phases can influence the activity and selectivity significantly. In the example shown here, significant amount of desirable butadiene is formed, which is not the case always. In the latter, we show how the crystal structure of the metal oxide support determines the selectivity and activity of noble metals supported on them in biomass conversion reactions. If time permitting, we will also show the results on catalytic oxidative dehydrogenation of ethyl lactate over simple and inexpensive TiO₂ under mild conditions in liquid-phase.

Figure 1. Conversion of butane and selectivities of various products as a function of different temperatures over a vanadate catalyst prepared in our laboratory.
Effect of rare earth doping on structural defects and redox properties of CeO$_2$/ZrO$_2$ based materials probed by \textit{in situ} Raman spectroscopy.

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Ceria (fluorite cubic structure, space group $Fm\overline{3}m$ ($O_h^5$)) has an exceptionally simple vibrational structure with one Raman active mode ($F_{2g}$) which is typically observed around 460 cm$^{-1}$ and is due to the symmetric breathing mode of O atoms surrounding each Ce$^{4+}$. As the $F_{2g}$ mode is only dependent on the oxygen movement, its band characteristics (width and position) are extremely dependent on the disorder induced in the oxygen ion sublattice of the oxide and is therefore sensitive to both Ce–O bond arrangements and lattice defects. Punctual defects exist even in pure CeO$_2$ (earlier attributed to non-stoichiometric conditions, \textit{i.e.} Ce$^{3+}$ presence) and can be caused by O relocation from the interior of tetrahedral cation sublattice to the (otherwise/ideally empty) interior of the octahedral cation sublattice, causing Frenkel type O vacancies that are counter-balanced by the interstitial O atoms occupying the interior of octahedral sites. The D$_1$ band ($\sim$620 cm$^{-1}$, spectrum (a)) is assigned to the occurrence such interstitial O atoms. Incorporation of Zr$^{4+}$ (i.r. of 0.84Å, vs 0.97Å for Ce$^{4+}$) results in lattice deformation and contraction manifested by a blue shift of $F_{2g}$ (458$\rightarrow$466 cm$^{-1}$) and strengthening of the D$_1$ band due to a larger extent of occurrence of Frenkel-type defects for the Ce$_{0.8}$Zr$_{0.2}$O$_2$ material. Doping of this material with RE$^{3+}$ ions results to (a) changes in the position and width of the $F_{2g}$ band (the position being dependent on the \textit{i.r.} of the RE$^{3+}$ ion) and (b) appearance of band D$_2$ caused by defects arising from doping (anionic lattice around RE$^{3+}$). The response of the \textit{in situ} Raman spectra under 5%H$_2$/He gas is suggestive of a lability of the interstitial O atoms that appear to be removed by H$_2$, judged from the pertinent lowering of the relative intensity of the D$_1$ band.

\textit{Acknowledgment.} Research supported by the RPF/THEPIS program (TECHNOLOGIA/THEPIS/0311(BE)/33).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure.png}
\caption{\textit{In situ} Raman spectra of Ce$_{0.8}$Zr$_{0.15}$RE$_{0.05}$O$_{2-\delta}$ materials (RE= La, Pr, Y, Nd) synthesized by the citrate sol-gel method at 480$^\circ$C under flowing 20% O$_2$/He (g). D$_1$,D$_2$: defect bands. Laser wavelength, 491.5 nm; laser power, 40 mW.}
\end{figure}
Modeling the structure and reactivity of Pt-ceria catalysts from ideal to realistic reaction environments

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Due to its high reducibility and oxygen storage capacity, ceria (CeO2) is extensively used as an active support for platinum-group metals in fuel-cell electrodes. Here we combine DFT+U simulations with ab-initio molecular dynamics, metadynamics, and umbrella sampling methods to provide insight into the surface chemistry opened by novel ceria catalysts with ultra-low Pt loading. The calculations are used to characterize the structure and the reactivity of the active sites in a wide range of compositions and environments, from ideal surfaces to complex nano-structured catalysts in the presence of liquid water at finite temperature. The simulations’ results are used for the interpretation of photoelectron spectroscopy and scanning tunneling microscopy measurements.

We start with the hydroxylation and reduction of ceria surfaces driven by molecular H2, and demonstrate the so-far unrecognized role of entropy on the reaction mechanism and kinetics. Our metadynamics calculations show that finite temperature effects alter the reaction mechanism, change the nature of the rate-limiting transition state, and decrease the activation temperatures for H2 dissociation by more than 25% (1).

We consider a variety of Pt-CeO2 systems in which Pt is either supported on or incorporated in the ceria lattice (2). We identify the thermodynamic conditions allowing for the dispersion and stabilization of specific Pt2+ and Pt4+ species on ceria surfaces. In particular, we show that Pt segregation to step edges leads to stable dispersions of single Pt2+ ions in planar PtO4 moieties incorporating excess O atoms and contributing to the oxygen storage capacity of ceria (3). We demonstrate the key role played by surface line defects and investigate the reactivity of different Pt sites towards hydrogen and methanol oxidation (3).

Finally, the distinct effects of liquid water, often present at electrodes in realistic conditions, on the surface chemistry of Pt-ceria catalysts are characterized on the basis of ab-initio molecular dynamics simulations.

Mesoporous materials are solids with specially ordered porous features on the nano-scale (2-50 nm). Ordered mesoporous materials can be classified according to their structure dimensions and pore geometry, e.g., either 2D-hexagonal (MCM-41) or 3D-cage-type (SBA-12 and -16) structures. By introducing transition metals (e.g. niobium, ruthenium or tin) into their structure the acid-base active centers are generated and these materials can be effective catalysts in oxidation reactions.

This work focuses on the oxidation of cyclohexene by using heterogeneous type nanocatalysts (SBA-12, SBA-16 and MCM-41) containing ruthenium, niobium and tin using microwave as a method of heating and acetonitrile as a solvent. The mixture of cyclohexene, acetonitrile, hydrogen peroxide and catalyst was transferred into microwave reaction vessel and treated in the Discovery microwave system under stirring at 318 K and pressure of 17 bars for 1, 2 and 3 hours. The temperature and pressure in the vessel have been controlled by program during the whole reaction time. The reactor content, taken at specified intervals, was analysed by using a Varian chromatograph GC3800.

All the obtained mesoporous molecular sieves were active catalysts for the oxidation of cyclohexene. The influence of reaction time, composition and structural/textural properties of the catalyst on the conversion of cyclohexene to the desired products was determined. The conversion of this substrate increased with time of reaction. The results of this reaction showed that diol and epoxide of cyclohexene were the main products of this reaction. The best results was obtained for Nb- containing MCM-41 catalyst: conversion of cyclohexene was ~40% and selectivity to main product (epoxide) ~100% after 3 h of reaction at 318K.

The application of microwave radiation contributed to obtain higher conversions of cyclohexene compared to the conventional heating and to shorten the reaction time. To conclude, the excellent catalytic performance of the Nb-containing mesoporous materials is due to the strength and amounts of Nb acidic sites in combination with wide pores, large surface area and relatively hydrophobic surface.
Application of functionalized mesoporous silica in adsorption processes

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Introduction
The ordered mesoporous silicas have been the subject of interests of many research groups. These materials display a number of attractive properties, among them the presence of pores of diameters ranging from 2-50 nm, high ordering of mesopores, well developed surface area (600-1000 m²/g) and nontoxicity [1-3]. Pure mesoporous materials show low chemical activity, which restricts their applications. Therefore, the surface of these materials can be functionalized by introducing the organic groups. Attractive structural characteristics and excellent alkaline properties exhibit amino-functionalized mesoporous molecular sieves. These kind of materials can be synthesized by the direct method or by the post-synthesis approach.

The aim of this study was to compare the sorption properties of amino-functionalized mesoporous materials such as SBA-15, SBA-16 and MCM-41 towards phenazone.

Experimental Section
Mesoporous silicas were synthesized by one-pot synthesis method. The obtained amino-functionalized mesoporous materials were characterized by low-temperature nitrogen sorption, X-ray and laser diffraction, transmission electron microscopy. Phenazone adsorption process was performed by solvent evaporation technique (5 mg phenazone/100 mg silica). Afterwards, desorption process of phenazone was studied in simulated gastric fluid and in pH 7.2 by using UV spectrophotometry at the maximum absorption of 263 nm.

Results and Discussion
Textural parameters calculated based on nitrogen adsorption/desorption isotherms indicate a decrease in the surface area and mesopores volume of amino-modified silica when compared with the pristine material. This implies that some mesopores were blocked by organic functional groups. It was found that the adsorption and desorption properties of phenazone were highly dependent on the pore size and structure of silica. The drug desorption profiles could be regulated by changing the textural parameters of mesoporous silica by functionalization with amine groups.

References
Supercharged Oxygen Storage in Nanoceria Revisited Using Hybrid Density Functionals

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Recent experiments have shown that the oxygen storage capacity (OSC) of nano-ceria is size [1, 2] and shape dependent [3], and a dramatically increased OSC has been measured for very small nanoparticles (d < 5 nm) [1]. Based on theoretical calculations, this effect has been suggested to originate from the adsorption and desorption of superoxo-ions at the corners and edges of initially partially reduced ceria nanoparticles, thereby "supercharging" them [4]. However, there remained a quantitative discrepancy between the theoretically predicted superoxo binding energy, and that deduced from experimental TPR data [1,2]. Bearing in mind that the accuracy of the binding energies calculated in Ref. [4] is likely to have been limited to some extent by the theoretical method that was used (PBE+U), we set out to refine and confirm those predictions using a higher level of theory.

To do so, we used the screened Coulomb hybrid density functional HSE06, as implemented in the VASP code, which is known to provide a significantly improved description both of ceria and of the O\textsubscript{2} molecule. We also used a modified HSE06 density functional, in which we have tuned the amount of exact exchange from the standard 25\%, which performs better for the electronic properties of bulk ceria, but leads to a small overestimation of the O\textsubscript{2} binding energy. Thus, while no single hybrid functional is yet capable of describing our system flawlessly, by combining results from both functionals, we are able to estimate binding energies for direct comparison with experimental data. The nanoparticles that were used in Ref. [4] are too large to be treated within the current computational method. Instead, we use a series of small stoichiometric, reduced and supercharged clusters (containing 4–10 Ce ions), which have been shown in a previous study to serve to exhibit similar supercharged oxygen chemistry to the larger ceria nanoparticles [5].

Our calculations show that, while stability trends between the stoichiometric, reduced and supercharged clusters are similar using the hybrid and the PBE+U functionals, the absolute values differ. In particular, the reduced clusters are significantly destabilized using the hybrid functional relative to PBE+U, whereas the stoichiometric and supercharged clusters are little affected. This effect results in a stronger adsorption energy for the O\textsubscript{2} molecules associated with the supercharged clusters than in the corresponding PBE+U calculations. Thus, these results provide support for the interpretation that the superoxo-ions are responsible for the dramatically increased OSC seen in experiments [1].

Density functional theory calculations have been used to explore NO\textsubscript{x} adsorption on perovskite oxides surfaces ATiO\textsubscript{3}(001) with A=Ca, Sr, Ba [1]. NO adsorbs weakly on all facets with no apparent A-ion dependence, whereas NO\textsubscript{2} adsorbs preferably over AO-terminated surfaces with adsorption energies that correlate with the ionization potentials of the alkaline earth atoms. Simultaneous adsorption of NO and NO\textsubscript{2} is found to substantially enhance the stability of the adsorbates owing to an oxide mediated electron-pairing mechanism. Stabilization is predicted also for NO/O\textsubscript{2} adsorption and it is suggested that presence of oxygen favors the formation of nitrite/nitrate pairs. It is found that the NO\textsubscript{x} adsorption properties can be modified by mixing alkaline earth cations in the perovskite framework. The results are put in context by comparison to NO\textsubscript{x} adsorption on the corresponding (001) facets of alkaline earth metal oxides and TiO\textsubscript{2}(110).

Relative stability and reducibility of CeO$_2$ and Rh/CeO$_2$ species on the surface and in the cavities of $\gamma$-Al$_2$O$_3$: a periodic DFT study

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The study reports the structure and stability of ceria units or small nanoparticle, Ce$_{13}$O$_{26}$ deposited on the (100) and (001) surfaces or incorporated in the cavities of $\gamma$-Al$_2$O$_3$, which is most often used as a support of CeO$_2$ species [1]. The deposition of a single Rh atom in some of the structures with a CeO$_2$ unit and Ce$_{13}$O$_{26}$ nanoparticle is also investigated.

The aim of our study is to help in rationalization of the experimental work of Duarte et al., who report for Rh/CeO$_2$/Al$_2$O$_3$ catalyst, that a reduced sample under oxidizing conditions contains significant fraction of Ce$^{3+}$ ions and only part of the Ce$^{3+}$ species are converted to Ce$^{4+}$ cations [2]. For all structures with deposited rhodium atom the calculations show electron transfer from rhodium to a cerium ion resulting in reduction of Ce$^{4+}$ to Ce$^{3+}$ and the oxidation of Rh$^0$ to Rh$^+$. Therefore, the formation of Rh$^+$ cation stabilizes the reduced cerium ions.

The periodic DFT calculations were performed with the exchange-correlation functional PW91 using Vienna Ab Initio Simulation Package (VASP). The valence wave functions were expanded to a plane wave basis with energy cut-off of 415 eV.

![Figure 1](image.png)

Figure 1. Selected optimized models of different structures with deposited Rh atom and ceria species on $\gamma$-Al$_2$O$_3$(100): a) deposited Rh ion and deposited one CeO$_2$ unit; b) deposited Rh and Ce$_{13}$O$_{26}$ nanoparticle. Rh ion is marked in indigo, Ce$^{3+}$ – cyan and Ce$^{4+}$ – green.

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Surface and texture properties of mesoporous silica modified with aluminum

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Introduction
Discovery of the ordered mesoporous silica is all-important for expanding the application of molecular sieve, because the well-developed surface area and pore volume, controlled pore size and very narrow pore size distributions enable the mesoporous material to be the valuable candidate for adsorption, separation, catalysis, drug delivery, etc. [1–3]. However, the pure siliceous framework limits the actual applications of mesoporous silica due to the lack of acid sites and ion-exchange capacity. Incorporation of aluminum and other transition metal ion into the amorphous walls of mesoporous silica materials is beneficial to improve their adsorption and catalytic activity, and the embodying aluminum into SBA-15, SBA-16, MCM-41 can be realized through post-synthetic and direct methods. Post-synthetic methods often block the pores of mesoporous silica partially thereby many efforts have been devoted to one-pot synthesis of Al-containing mesoporous silica. Nevertheless, direct synthesis of e.g. Al-SBA-15 is difficult because free aluminum species such as Al$^{3+}$ only exist in cationic form and the Al–O–Si bonds are easy to dissociate under strongly acidic conditions. So, it is still a challenge to find a simple one-step route to prepare the Al-incorporated SBA-15, SBA-16, MCM-41.

The aim of our study was the modification of mesoporous silica materials (such as MCM-41, SBA-15, SBA-16) with aluminum and their physicochemical characterization.

Experimental Section
Aluminum containing mesoporous materials MCM-41, SBA-15 and SBA-16 were synthesized by hydrothermal method with tetraethyl orthosilicate as the silica source and different surfactants (cetyltrimethylammonium bromide, triblock copolymers: Pluronic P123, Pluronic F127) as templates. Aluminum isopropoxide was used as precursor of metal. The Si/Al atomic ratio in the gels was 30 and 60. Structure and surface properties of the materials obtained were characterized in detail by low-temperature nitrogen sorption, X-ray diffraction, transmission electron microscopy, laser diffraction and ultraviolet-visible spectrophotometry.

Results and Discussion
XRD patterns confirmed well-ordered arrangement of mesopores in all samples used in this study. All pure silicas and aluminum modified samples showed well-developed surface area and high pore volume. Introduction of aluminum ions into the mesoporous silicas resulted in an increase in surface area. Furthermore, the aluminum-modified samples contained particles of greater size than the pure samples of SBA-15, SBA-16 and MCM-41. SBA-16 type silica of regular structure contains larger particles than SBA-15 and MCM-41 samples showing hexagonal ordering.

References
The syngas to methanol reaction on the (0001) surface of doped Cr$_2$O$_3$

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The rapidly increasing world population and urbanisation has led to the significant development of the automotive and transport industries, placing a huge burden on the supply of natural resources. A renewable fuel is thus desirable to reduce the strain on non-renewable sources, which is also environmentally friendly to reduce the concentration of atmospheric pollutants. The use of degradable bio-organic matter has attracted much interest as a renewable energy source since it can be reformed to biogas that is subsequently used as precursor to biofuel production. Biogas is primarily methane gas (CH$_4$) and has attracted substantial interest within the area of ‘green chemistry’, since it can be used to create synthetic gas (syngas, CO + H$_2$), a precursor to methanol (CH$_3$OH) and higher alkane (biodiesel) production.[1,2]

Density functional theory (DFT) calculations will be used to investigate a range of dopants that promote surface oxygen vacancy formation (O$_{\text{vac}}$), but not too strongly as to suppress the well-known Mars-Van Krevelen mechanism. The calculations indicate that the O$_{\text{vac}}$ energies for Al-, Fe-, La-, Ni-, and Zr- doped Cr$_2$O$_3$ surfaces are within a suitable range to promote O$_{\text{vac}}$, and potentially improve methanol synthesis compared to the pure Cr$_2$O$_3$ surface. The reaction profiles for the syngas to methanol reaction on each doped surface were developed by using the lowest energy intermediate structures leading to methanol formation. The profiles indicate that the formation of the formaldehyde intermediate is difficult on all surfaces and perhaps the rate limiting step. Water formation was found to be inevitable as a bi-product at some stage along the reaction profile on each of the doped surfaces. The energy to remove water from the surface lies with the origin of the oxygen species from either the CO source or surface O atoms, as the C=O bond is difficult to break while surface O atoms are more favourable. This, not only impacts the thermodynamics for methanol selectivity and thus yield, but also indicates that a higher molar ratio of H$_2$ is required to drive the reaction forward to produce methanol.


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Complete Hydrocarbons Oxidation over Au, Pd and Pd-Au Catalysts Supported on Y-doped Ceria

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The detoxification of hydrocarbon air pollutants remains one of the global environmental problems. Recently, considerable attention was paid on the complete oxidation of volatile organic compounds over nanosized gold catalysts. The predominant opinion concerning Au catalysts on reducible supports is for Mars–van Krevelen redox mechanism with active oxygen supplying by the support. The key factors for high catalytic activity are the gold dispersion and the support features, in particular the redox properties. Benzene is a harmful air pollutant having a very stable molecule. It was chosen as a probe and the present study was focused on complete benzene oxidation (CBO) on Au catalysts supported on ceria with light Y-doping (1 to 7.5 wt.% of Y\textsubscript{2}O\textsubscript{3}, correspondingly 1.5 to 11.0 at.% of Y). Two series of mixed supports were synthesized by co-precipitation (CP) and by impregnation (IM). The gold catalysts (3 wt.% Au) were prepared by deposition-precipitation (DP) method. The catalysts were characterized by XRD, HRTEM-HAADF, TPR and Raman spectroscopy. Special attention was paid on the air pretreatment conditions – it was established higher CBO activity after pretreatment at 350°C as compared to 200°C. The TPD experiments performed with O\textsubscript{2} adsorbed at these temperatures allowed to conclude that the reason for the improved CBO activity after pretreatment at 350°C can not be related to the higher oxygen uptake. Most probably the explanation is related to the better active sites cleaning by CO\textsubscript{2} removal (QM analysis). The catalytic behavior in CBO over the studied Au catalysts did not differ very significantly. The highest was the CBO activity of the Au catalyst on synthesized by IM ceria support doped by 1 wt.% of Y\textsubscript{2}O\textsubscript{3}. The supports with 1 wt.% dopant, prepared by IM or CP were chosen for further investigation of Au (3 wt.%), Pd (1 wt.%%) and PdAu (1 wt.% of Pd over already prepared Au catalysts). The mono- and bi-metallic catalysts were characterized by XRD, XPS and TPR. The test of CBO and complete propene oxidation (CPO) (propene was chosen as a probe molecule for combustion of aliphatic hydrocarbons) were performed using pretreatment in air at 350°C. In both reactions, CBO and CPO, the highest catalytic activity and good stability was established over Pd-Au catalyst on IM prepared Y-doped ceria (1 wt.% Y\textsubscript{2}O\textsubscript{3}). The results of 100% propene complete oxidation at 180°C and especially the total benzene combustion at temperature as low as 150°C (see the figure) makes this Pd-Au catalyst promising for practical application. Relationships between structure, redox and catalytic properties were sought.

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Synthetic routes for obtaining SBA-15 mesoporous matrix modified with acidic or basic functional groups

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Mesoporous matrixes of SBA-15 type are very interesting materials due to their structural properties such as ordered structure, large surface area and the presence of mesopores. These properties of ordered silicas can be controlled with respect to the synthesis conditions [1], leading to the materials used mainly in catalysis and adsorption [2].

The main purpose of the study was to design the efficient synthesis methods for obtaining SBA-15 ordered mesoporous silicas and their modified counterparts containing basic or acidic moieties, which would find the application in the catalysis.

Synthesis of SBA-15 materials were performed using tetraethyl orthosilicate (TEOS) as a silica source and triblock copolymer Pluronic P123 as a template. The obtained materials were modified with amino groups (from Z-6020 or Z-6032 aminosilanes) in order to generate basic active centres or with thiol groups (from mercaptopropyltrimethoxysilane) to generate acidic active centres. The modification of the obtained mesoporous materials was performed by two different methods. One of them was co-condensation, where the functional groups were introduced into the solution at the stage of the molecular sieve synthesis. The second route of the modification was grafting, where amino or thiol groups were introduced onto the surface area of the previously obtained silica.

To determine the physicochemical properties of obtained materials several techniques were used, namely: X-ray diffraction (XRD), low temperature nitrogen sorption measurements, FT-IR spectroscopy, thermal analysis, elemental analysis and transmission electron microscopy (TEM). The obtained results proved the mesoporosity, ordered structure and the presence of functional groups in all tested samples.

Additionally, selected materials containing amino groups were tested for their catalytic activity in the Knoevenagel condensation, where they were used as basic catalysts in the reaction between benzaldehyde and ethyl acetoacetate. The obtained results confirmed the possibility of using this type of materials as basic catalysts.

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Ordered mesoporous materials of MCM-41 type – synthesis, modification and characterization of their physicochemical and catalytic properties

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We present results of our studies on synthesis and modification procedures for obtaining purely siliceous ordered mesoporous materials and their counterparts modified with heteroatoms. Our main research area was the development of simple and efficient methods for synthesis of MCM-41 materials and its modification with organic compounds containing nitrogen or sulphur atoms.

Heteroatoms were introduced by two different procedures, namely "one-pot" synthesis or post-synthetic grafting. In the next step of our studies the received formulations were evaluated in the terms of physicochemical properties. For this purpose X-ray diffraction (XRD) technique (the range of 2θ angles: 0,6-8,0°), low-temperature nitrogen adsorption-desorption measurements, transmission electron microscopy (TEM) and infrared spectroscopy (FT-IR) were applied. Moreover, selected samples were subjected to the elemental analysis in order to confirm an incorporation of heteroatoms into/onto the siliceous matrix. In addition, selected MCM-41 materials, containing amino groups introduced by grafting, were tested as catalysts in the Knoevenagel condensation.

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Role of Cu/Mn Molar Ratio and Gold Addition on the Performance of Alumina Supported Cu-Mn Catalysts for WGSR

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Introduction: The Water-Gas Shift Reaction (WGSR) is a well established industrial process for hydrogen generation by conversion of CO in hydrogen-rich gas streams. The need of high-purity hydrogen for fuel cell applications stimulates a great activity in the design of novel, highly active and stable WGS catalysts. Copper is often used as an active component in low-temperature (LT) WGS catalysts. Recently, we have reported that Cu-Mn spinel oxide demonstrated favorable characteristics and catalytic properties for WGSR [1]. Due to their good redox property, these mixed oxides play an important role in the activation of water. The aim of present study was to develop cost-effective and catalytically efficient formulations based on γ-Al₂O₃ modified with a superficial fraction of Cu–Mn mixed oxides. The effect of Cu/Mn molar ratio (2:1 or 1:5) and the role of Au addition on the structural and catalytic properties were examined.

Experimental: The samples were prepared by the wet impregnation method. Commercial γ-Al₂O₃ was used as support. The impregnation with mixed solutions of copper and manganese nitrates (20 wt. % active phase) was performed at 80 °C for 12 hours. The samples were dried at 120 °C for 10 h and calcined at 450 °C for 4 hours. Au samples (2 wt. %) were synthesized by deposition-precipitation method.

Results and discussion: Catalytic tests revealed that WGS activity is governed not only by the presence of Au, but also by the Cu-Mn molar ratio (Fig. 1). Higher activity was demonstrated by the sample with higher Cu content, i.e. that with ratio 2:1. Both gold-containing catalysts are more active than the corresponding supports. The highest catalytic activity among the studied catalysts was shown by the Au catalyst on support with Cu/Mn ratio 2:1. The characterization of as-prepared and used in WGSR samples by means of BET, XRD, HRTEM/HAADF, XPS, EPR and TPR was performed in order to explain the relationship between structure, reduction behaviour and WGS activity.

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References: